L Number	Hits	Search Text	DB	Time stamp
1	111	((annealing or crystallizing) with PZT) same (oxygen or oxidizing)	USPAT; US-PGPUB	2003/05/17 14:32
2	59	(((annealing or crystallizing) with PZT) same (oxygen or oxidizing)) and @ad<19991029	USPAT; US-PGPUB	2003/05/17 15:20
3	7	((annealing or crystallizing) with PZT) same (oxygen or oxidizing)	EPO; JPO; DERWENT; IBM_TDB	2003/05/17 14:36
4	3657	438/3,240,253,381,396.ccls.	USPAT; US-PGPUB	2003/05/17 15:21
5	792	438/3,240,253,381,396.ccls. and PZT	USPAT; US-PGPUB	2003/05/17 15:21
6	409	(438/3,240,253,381,396.ccls. and PZT) and oxygen and (crystallizing or annealing or heating)	USPAT; US-PGPUB	2003/05/17 15:22

L Number	Hits	Search Text	DB	Time stamp
1	111	((annealing or crystallizing) with PZT) same (oxygen or oxidizing)	USPAT; US-PGPUB	2003/05/17 14:32
2	59	(((annealing or crystallizing) with PZT) same (oxygen or oxidizing)) and @ad<19991029	USPAT; US-PGPUB	2003/05/17 14:13
3	7	((annealing or crystallizing) with PZT) same (oxygen or oxidizing)	EPO; JPO; DERWENT; IBM TDB	2003/05/17 14:36

US-PAT-NO: 6066581

DOCUMENT-IDENTIFIER: US 6066581 A

TITLE: Sol-gel precursor and method for formation of ferroelectric materials for integrated circuits

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Application Filing Date - AD (1):
19960725

Brief Summary Text - BSTX (76):
In providing materials, including **PZT,** for high frequency (microwave) applications, **annealing** is beneficially carried out in an atmosphere comprising **oxygen** and ozone, and in the presence water vapour, at lower temperature, i.e. .about.500.degree. C. Under these conditions uniform growth of fine grained polycrystalline material occurs, and grain sizes growth above about 20 nm were not observed. Superior high frequency characteristics were observed for material characterized by uniform small grain sizes.

Brief Summary Text - BSTX (100):
The layer of as-deposited material was first dried at 100.degree. C. for about 30 seconds and then heat treated at low temperature, i.e. below .ltoreq.450.degree. C. for about 30 to 90 seconds, to drive off volatile organic components and to form an amorphous layer. To build up a layer of the required thickness, several thin layers were sequentially deposited and heat

treated. The resulting amorphous layer was then annealed by a rapid thermal annealing (RTA) process at above 450.degree. C., and up to 650.degree. C. in an annealing atmosphere comprising **oxygen,** preferably in the presence of water vapour, for 30 seconds to several minutes. Water vapour was conveniently introduced into the **annealing** atmosphere of the rapid thermal anneal (RTA) system during the **annealing of the PZT** by passing **oxygen** (O.sub.2) through a double bubbler containing purified deionized (DI) water, so that the **oxygen** was saturated with water vapour, e.g. using a gas flow rate of about 2 L/min. Ozone is preferably added to the **annealing** atmosphere to speed up oxidation. The latter annealing atmosphere was found to be beneficial for annealing by rapid thermal processing, where processing time is relatively short compared with conventional furnace annealing processes. Beneficially, the first heat treatment is also carried out in the same annealing atmosphere comprising **oxygen,** ozone and water vapour.

Brief Summary Text - BSTX (108):

It has generally been observed that the PZT made by known conventional processes shows dispersion at high frequencies above .about.100 MHz, above which frequency the dielectric constant of PZT was observed to drop a very low value<10. Thus, although BST generally requires higher temperature processing than PZT, it has been considered a ferroelectric material of choice for high frequency applications in the microwave (GHz) frequency range, e.g. for capacitors for GaAs integrated circuits. Nevertheless, as described in copending patent application Ser. No. 08-410,695 to Chivukala et al., filed Mar. 21, 1995 and now abandoned entitled "Ferroelectric dielectric material for integrated circuit applications at microwave frequencies" which is incorporated herein by reference, a method of preparing **PZT** with improved high frequency characteristics by **annealing in oxygen** and ozone, preferably in the presence of water vapour, at low temperature provide a **PZT** layer having a fine grained structure which shows no significant dispersion up to at least 10 GHz.

Brief Summary Text - BSTX (112):

The effect of the introduction of water vapor in the annealing ambient on the stress and crystallization kinetics was studied in the related work reported in the above mentioned copending patent application. The initial focus of this effort was a reduction of the crystallization temperature of the PZT from.about.650.degree. C. to<500.degree. C. However, this led to the discovery that the presence of water vapour during annealing has a significant effect in reducing film stress. The introduction of water vapour by bubbling O.sub.2 or an O.sub.2 /O.sub.3 mixture through purified, de-ionized water into the rapid thermal anneal (RTA) system during the **annealing of the PZT** resulted in crystallization at about 450.degree. C., with improved or comparable physical properties and electrical properties. In particular, annealing at low temperature 450-500.degree. C. in the presence of water vapour, as compared to the standard process in dry **oxygen,** resulted in a lower tensile stress (2-3.times.10.sup.9 dyne/cm.sup.2) compared to the tensile stress values of 1-2.times.10.sup.10 dyne/cm.sup.2 that are seen in films annealed in dry **oxygen** ambient at.gtoreq.650.degree. C. Generally, it is found to be advantageous if the film stress values be kept as low as possible in order to avoid the problems associated with the peeling of the films and adhesion to other materials. Nevertheless, it is believed that the film stress is remains high relative to bulk material. No significant correlation was found between the high frequency response and the film stress in the samples.

Detailed Description Text - DETX (75):

The solutions of strontium nitrate and barium acetate were mixed, and then mixture was added to the titanium iso-propoxide solution. The resultant solution was spin coated onto a substrate and heat treated as described for formation of **PZT,** with the exception that the **annealing** step was carried out at a higher temperature, between 650.degree. C. and 850.degree. C., and preferably in an atmosphere comprising **oxygen**/ozone and water vapour using rapid thermal annealing, as described above for other materials.

US-PAT-NO: 5905278

DOCUMENT-IDENTIFIER: US 5905278 A

TITLE: Semiconductor device having a dielectric film and a fabrication process thereof

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Application Filing Date - AD (1):
19970729

Brief Summary Text - BSTX (23):
In relation to the diffusion barrier, it should be noted that the conventionally used Ti layer is found to be not effective for interrupting the diffusion of Si from the plug 115 to the lower capacitor electrode 110. Further, the use of a Ti layer in the lower capacitor electrode 110 causes the problem of diffusion of Pb and **oxygen** atoms from the PZT film 111 to the lower capacitor electrode 110 at the time of the RF sputtering process used for forming the PZT film 111. It should be noted that the RF sputter deposition of the PZT film 111 is conducted under an **oxidizing** atmosphere that contains O.sub.2. A similar problem of **oxygen** diffusion occurs also when applying an **annealing** process to the **PZT** film 111 after a formation thereof. It should be noted that such an **annealing** process is essential for improving the quality of the **PZT** film 111 and has to be conducted in an **oxidizing** atmosphere, while a material such as Pt or Ti does not function as an effective diffusion barrier against **oxygen** atoms. Thus, the **oxygen** atoms readily reach the conductive plug

115 underneath the electrode 110 and cause an extensive formation of silicon oxide at the interface between the plug 115 and the electrode 110. When this occurs, there is a substantial risk that the ohmic contact between the electrode 110 and the conductive plug 115 is lost.

US-PAT-NO: 6194228

DOCUMENT-IDENTIFIER: US 6194228 B1

TITLE: Electronic device having perovskite-type oxide film, production thereof, and ferroelectric capacitor

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Application Filing Date - AD (1):
19981021

Detailed Description Text - DETX (11):
The **PZT** film obtained by repeated spin coating and thermal decomposition is crystallized by heat treatment (such as lamp **annealing) in an oxidizing** atmosphere containing **oxygen**. This heat treatment may be carried out in an annealing apparatus having a capacity of about 20 liters, by supplying **oxygen** at a flow rate of about 5 L/min, with the temperature raised to 650.degree. C. at a rate of 1.degree. C./s, kept at 650.degree. C. for 30 minutes, cooled to 200.degree. C. over a period of 30 minutes, and finally cooled naturally.

Detailed Description Text - DETX (41):
The thus obtained **PZT** film is crystallized by heat treatment (such as lamp **annealing) in an oxidizing** atmosphere containing **oxygen**. This heat treatment may be carried out in such a way that the temperature is raised to 650.degree. C. at a rate of 100.degree. C./s and kept at this temperature for 2 minutes.

In this way there is obtained a polycrystalline PZT film 6.

US-PAT-NO: 6146905

DOCUMENT-IDENTIFIER: US 6146905 A

TITLE: Ferroelectric dielectric for integrated circuit applications at microwave frequencies

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Application Filing Date - AD (1):
19990617

Brief Summary Text - BSTX (17):
In preparing **PZT** films having high frequency performance above 1 GHz, a low temperature method was employed, for example a sol-gel process, comprising **annealing,** by rapid thermal processing, in an **oxygen** and ozone containing atmosphere, and preferably in the presence of water vapour. In addition to providing PZT films with high dielectric constant >300 and low film stress, it was discovered that the frequency response of the PZT was extended into the GHz range relative to the roll-off in dielectric constant which occurs at about 100 MHz in bulk ceramic PZT. Consequently, the usefulness of this material as a ferroelectric dielectric, is extended for use, e.g. for capacitors for integrated circuits operable at microwave frequencies. In other applications, these fine grained polycrystalline PZT may be used for high frequency surface acoustic wave (SAW) devices having low mechanical loss.

Detailed Description Text - DETX (2):

In a method of forming a ferroelectric dielectric for a capacitor structure according to a first embodiment of the present invention, a ferroelectric capacitor structure was formed on an integrated circuit substrate comprising a semiconductor silicon wafer. A bottom electrode of a capacitor was defined on the substrate. The bottom electrode comprises a single conductive layer, or alternatively comprises a multilayer structure including a barrier layer and an adhesion layer. In the present example a bottom electrode was formed from sputtered platinum. A layer of lead zirconate titanate (PZT) was then formed on the bottom electrode as described in the above mentioned copending U.S. patent application Ser. No. 08-348848, using a known spin-on liquid process to apply to the substrate a metallorganic sol-gel precursor comprising constituents of the ferroelectric material, i.e. an inorganic lead compound, and zirconium and titanium alkoxides in the desired proportions, e.g. to provide a 40:60 ratio of zirconium to titanium. A layer of the required thickness was obtained by sequentially depositing and heat treating several thin layers. Each layer of as-deposited material was heat treated at low temperature, i.e. below .ltoreq.450.degree. C. for about 90 seconds, to drive off volatile organic components and to form an amorphous layer. The resulting amorphous layer was then annealed by a rapid thermal annealing (RTA) process at 450.degree. C. or higher, in an annealing atmosphere comprising **oxygen**, preferably in the presence of water vapour, for 300 seconds. Water vapour was conveniently introduced into the **annealing** atmosphere of the rapid thermal anneal (RTA) system during the **annealing of the PZT** by passing **oxygen** (O.sub.2) through a double bubbler containing purified deionized (DI) water, so that the **oxygen** was saturated with water vapour, e.g. using a gas flow rate of about 2 L/min. Ozone is preferably added to the **annealing** atmosphere to speed oxidation.

Detailed Description Text - DETX (8):

In related work reported in the above mentioned copending Patent Application, the effect of the introduction of water vapor in the annealing ambient on the stress and crystallization kinetics was studied. The initial focus of this effort was a reduction of the crystallization temperature of the

PZT from .about.650.degree. C. to <500.degree. C. However, this led to the discovery that the presence of water vapour during annealing has a significant effect in reducing film stress. The introduction of water vapour by bubbling O.sub.2 or an O.sub.2 /O.sub.3 mixture through purified, de-ionized water into the rapid thermal anneal (RTA) system during the **annealing of the PZT** resulted in crystallization at about 450.degree. C., with improved or comparable physical properties and electrical properties. In particular, annealing at low temperature 450-500.degree. C. in the presence of water vapour, as compared to the standard process in dry **oxygen,** resulted in a lower tensile stress (2-3.times.10.sup.9 dyne/cm.sup.2) compared to the tensile stress values of 1-2.times.10.sup.10 dyne/cm.sup.2 that are seen in films annealed in dry **oxygen** ambient at .ltoreq.650.degree. C. Generally, it is found to be advantageous if the film stress values be kept as low as possible in order to avoid the problems associated with the peeling of the films and adhesion to other materials. Nevertheless, it is believed that the film stress is remains high relative to bulk samples. Differences in the thermal expansion coefficient of the ferroelectric dielectric film and the substrate contributes to the stress levels in thin films. No significant correlation was found between the high frequency response and the film stress in these samples.

Detailed Description Text - DETX (31):

In another set of **PZT** samples prepared under different conditions, the effect of **annealing** in wet and dry **oxygen,** with and without ozone were compared. A bottom electrode comprising 2000 .ANG. platinum was deposited, followed by a blanket layer of 1800 .ANG. PZT, and a top electrode comprising 1000 .ANG. platinum patterned by a lift off technique. The PZT was deposited by two coatings, each of which were annealed for 90 seconds at 450.degree. C., followed by a third coating and an final anneal at 450.degree. C. for 5 minutes. Dielectric constants were measured as shown in Table I.